

unsorted material not showing the effects of running water or anything of that sort. I would strongly suspect that phosphate is present, but I am quite sure that it is not as much as an order of magnitude higher than in other meteorites.

DR. BRITTON CHANCE (University of Pennsylvania): I read Dr. Urey's speculation about hydrogen peroxide being the initial biological oxide. You may be interested to know baker's yeast is able to exist on  $H_2O_2$ . It is able to accomplish most of the intercellular oxidations which are usually done by the enzymes that work with oxygen.

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## THE HISTORY OF OCEAN WATER AND ITS EFFECT ON THE CHEMISTRY OF THE ATMOSPHERE

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During the past fourteen years we have passed a number of milestones on the way toward a satisfactory theory for the chemical evolution of ocean water. In 1951 Rubey (1951) introduced the concept of "excess volatiles" and showed that these constituents have almost certainly been added gradually to the atmosphere and oceans from the interior of the earth. In 1952 Barth (1952) introduced the concept of the residence time of ions in the oceans; he showed that all cations—with the possible exception of sodium—have residence times which are a small fraction of earth history, and that the oceans should be regarded as transitory rather than as permanent repositories for cations. Barth's (1952) conclusions have been confirmed and extended by Goldberg and Arrhenius (1958) and by Goldberg (1963).

The traditional view that the pH of the oceans is largely buffered by the carbonate system was challenged in 1961 by Sillén in a paper which must be regarded as a turning point in chemical oceanography. Sillén pointed out that silicates almost certainly also act as pH buffers, and that the large concentration of  $Na^+$  in the oceans today virtually provides a pH-stat for ocean water. Although the experimental underpinnings for Sillén's concepts are still not entirely secure, the result of Hemley's (1959, 1961, 1964) work on alkali-alumina-silica-water systems strongly supports the importance of many of the controlling reactions suggested by Sillén.

This paper is essentially a continuation and extension of Sillén's approach to the factors which control the chemistry of ocean water at present. I believe that we are sufficiently close to an understanding of these controls that we can employ them together with stratigraphic data to set some limits on the variations of the chemical composition of ocean water in the past. These limits in turn set restraints on the chemical composition of our atmosphere in the past, and a definition of these limits is the main object of this paper.

*Present Controls on the Composition of Ocean Water.*—In a system in dynamic equilibrium, input is balanced by outflow. The input into the oceans consists largely of dissolved and particulate matter transported by streams and by fresh ground water, and of volcanic and hot spring material introduced directly into the oceans. The response of these inputs to contact with ocean water should give us

valuable information regarding the mechanism of their ultimate removal from the ocean reservoir.

The first reaction of river sediment with ocean water involves extensive base exchange. Calcium, which usually predominates over the other cations in river water, is exchanged for  $Mg^{+2}$ ,  $Na^{+}$ , and  $K^{+}$  on contact with ocean water. This has been demonstrated by Carroll and Starkey (1960), who studied base exchange processes on a number of clays in contact with ocean water, and by Potts (see W. D. Keller, 1963), who studied the behavior of Mississippi River clays in contact with ocean water. In both studies it was found that base exchange was completed in a few tens of hours, a time which is clearly very short compared to the time of contact of clays entering the oceans from rivers.

The second reaction of river sediments with ocean water consists of the reconstitution of degraded illites and chlorites; this involves an increase in the potassium and magnesium content of these minerals, respectively, as has been shown by Powers' study (1959) of sediments in the James River estuary and by Nelson's study (1963) of sediments in the Rappahannock river. Such reconstitution reactions also appear to be completed in a period of time which is short compared to the contact time of these minerals with ocean water.

The third reaction appears to involve the formation of new clay minerals altogether. The reality of such processes has been widely debated during the past decade, and I feel that sufficient evidence is now available to suggest strongly that some clay minerals in ocean sediments are authigenic. In the long-term experiments of Whitehouse and McCarter (1958), no new mineral phases were formed by leaving kaolinite and illite in contact with sea water for periods up to 5 years. But samples of montmorillonite reacted in part to form new illitic and chloritic phases.

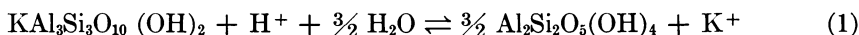
These laboratory results are in good agreement with those of a study by Johns (1963) of the mineralogy of sediments entering the Gulf of Mexico at Rockport, Louisiana. Johns (1963) found that the montmorillonite content of his sediments decreased seaward at the expense of illite and chlorite. The mineralogy of the finest-grained sediment fraction was most strongly affected. Although Whitehouse and McCarter's (1958) experiments can be criticized because they did not control the composition of their water samples, and Johns' (1963) mineral distribution pattern might have been affected by factors other than the reaction of river clays with ocean water, the balance of the evidence seems to point toward some reaction of montmorillonite with sea water to produce illite and chlorite in times which are still small compared to the exposure time of most river sediments to ocean water.

Recent studies of the K-Ar age of oceanic illites by Hurley *et al.* (1963) have shown, however, that the major portion of illite now at the ocean-sediment interface is detrital, and this conclusion is amply reinforced by Biscaye's study (see K. K. Turekian, 1964) of the distribution of clay minerals on the floor of the Atlantic Ocean and its relationship to the mineralogy of the sediment load of rivers which feed into the various parts of the Atlantic basin. Although the fraction of authigenic clays on the floor of the Pacific Ocean may be higher than on the floor of the Atlantic (E. D. Goldberg, 1963), it still remains that a large fraction of the clay minerals in the oceans as a whole are probably detrital rather than authigenic.

The behavior of the clay minerals on entering the oceans indicates that they approach equilibrium at least in part with the oceans. It seems likely that the

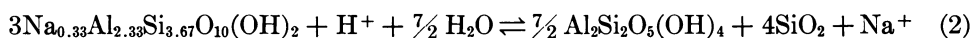
volume of sediment which has been in contact with the oceans has a weight many times that of the present oceans, and that therefore the mineralogy of sediments in turn should have exercised a series of restraints on the chemical composition of ocean water throughout geologic time.

Hemley (1959, 1961, 1964) has studied portions of the systems  $K_2O-Al_2O_3-SiO_2-H_2O$  and  $Na_2O-Al_2O_3-SiO_2-H_2O$  at temperatures between 300 and 600°C. His data on the equilibrium between muscovite and kaolinite, and between soda-montmorillonite and kaolinite, are particularly pertinent to the problem at hand, although the extrapolation of his data down to oceanic temperatures is uncomfortably long. His data for the reaction



suggest that the ratio  $a_{K^+}/a_{H^+}$  in a solution in equilibrium with these minerals should be  $10^{6.0 \pm 0.5}$  at 25°C.

His data for the reaction



suggest that the ratio  $a_{Na^+}/a_{H^+}$  in a solution in equilibrium with soda-montmorillonite, kaolinite, and quartz should be  $10^{7.0 \pm 0.5}$  at 25°C. In the present oceans

$$\frac{a_{K^+}}{a_{H^+}} = \frac{\gamma_{K^+}m_{K^+}}{a_{H^+}} = \frac{0.68 \times 0.01}{10^{-8.1}} = 10^{5.9}$$

and

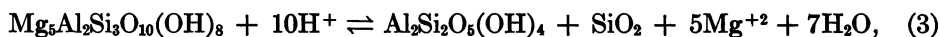
$$\frac{a_{Na^+}}{a_{H^+}} = \frac{\gamma_{Na^+}m_{Na^+}}{a_{H^+}} = \frac{0.68 \times 0.53}{10^{-8.1}} = 10^{7.7}.$$

[Note: The values of the activity coefficients are those proposed by Garrels and Thompson (1962).] The agreement between the predicted and actual value of  $a_{K^+}/a_{H^+}$  is excellent. The difference between the predicted and actual value of  $a_{Na^+}/a_{H^+}$  is greater, though possibly within the limits of error of the extrapolation of Hemley's data to low temperatures. Oceanic montmorillonites almost certainly are not pure soda-montmorillonites, and it is not known what effect the various compositional variables will have on the equilibrium value of the ratio  $a_{Na^+}/a_{H^+}$ . It is also possible that the undersaturation of most ocean water with respect to quartz is in part responsible for the apparently high value of  $a_{Na^+}/a_{H^+}$  in ocean water in contact with montmorillonite and kaolinite.

The general agreement between the values of these cation ratios in the pure system and in the oceans reinforces the concept that the oceans are at least approximately in equilibrium with illite, soda-montmorillonite, and kaolinite. Magnesium delivered to the ocean by rivers seems to be removed mainly via base exchange on montmorillonite and by the formation of chlorite. In the absence of data for reactions such as

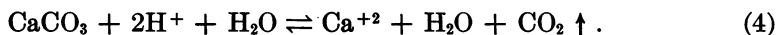
	millimoles liter		millimoles liter
Na <sup>+</sup>	480.80	Cl <sup>-</sup>	560.70
Mg <sup>+2</sup>	54.78	SO <sub>4</sub> <sup>=</sup>	28.84
Ca <sup>+2</sup>	10.46	HCO <sub>3</sub> <sup>-</sup>	2.38
K <sup>+</sup>	10.18	CO <sub>3</sub> <sup>=</sup>	0.27
Sr <sup>+2</sup>	0.10	Br <sup>-</sup>	0.85

FIG. 1.—The concentration of the major components of normal sea water.



we can only infer that if ocean water is in equilibrium with kaolinite and with chlorite of the composition  $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ , then the ratio  $a_{\text{Mg}^{+2}}/a_{\text{H}^+}^2$  will be fixed by the equilibrium constant for reaction (3).

No such equation can apparently be written for a calcium silicate which is stable in ocean water. The activity of  $\text{Ca}^{+2}$  may be controlled in part by base exchange reactions, but seems largely to be controlled by carbonate equilibria. Perhaps the most interesting of these is represented by the equation



In a solution saturated with respect to calcite and at a fixed pH, the product of the activity of calcium and the pressure of  $\text{CO}_2$  in the atmosphere is fixed. The value of the individual terms in this product for the ocean-atmosphere system can best be understood in terms of the kinetics of this system, which will be described shortly.

The reactions which I have proposed as controls on the concentration of the major elements in sea water look appealing, but I would like to acknowledge that the model is open to several criticisms before exploring its implications for the history of the oceans and of the atmosphere. The most obvious class of criticisms deals with the nonequilibrium aspects of the atmosphere-ocean system. There are, first of all, too many minerals present in ocean sediments. Among the potash-containing minerals, phillipsite and glauconite are known to be forming on the sea floor (G. O. S. Arrhenius, 1963). Although the stability relations of phillipsite at 25°C are not known, it seems reasonably certain that phillipsite can be in equilibrium with illite and kaolinite only in environments supersaturated with respect to quartz. It seems likely that this is true in many oceanic sediments (R. Siever, K. C. Beck, and R. A. Berner, 1965) and that the excess of silica activity required to make phillipsite a stable mineral phase is rather small. However, the activity of silica in solution demanded by the stable coexistence of gibbsite and kaolinite, for instance, is considerably smaller than the activity of silica in equilibrium with quartz. It is well known that ocean water in some areas is, in fact, highly depleted of  $\text{SiO}_2$ , mainly due to the activity of diatoms in the photic zone. The rather highly variable activity of  $\text{SiO}_2$  in ocean water may, therefore, be responsible for the appearance of several of the incompatible mineral phases in ocean sediments (R. M. Garrels, 1965).

There is little doubt, therefore, that the sea-water-sediment system is not completely at equilibrium, but perhaps a more fundamental criticism has its origin in the observation that the residence time of many elements in ocean water is small. It might be asked how much of the chemistry of the oceans depends on the kinetics of a variety of physical processes, and inorganic and biochemical reactions rather than on the equilibrium conditions described above.

Both objections can be answered in part by emphasizing that the correspondence between equilibrium conditions and the state of the oceans is sufficiently close to warrant the acceptance of the equilibrium model as a first approximation. But it looks as if kinetic factors must be taken into account at least to explain the carbonate chemistry of the oceans.

*The Composition of the Oceans in the Past.*—We can now set our model in motion. The simplest sort of motion consists of allowing water to evaporate from the oceans

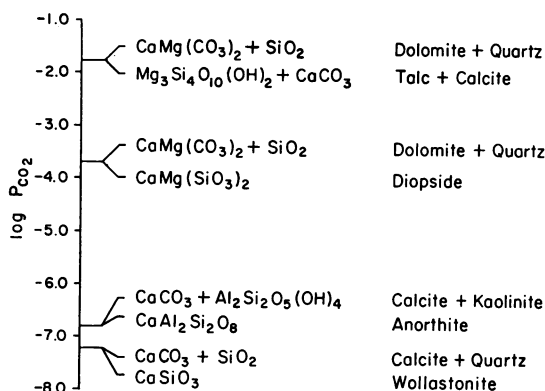


FIG. 2.—Equilibrium  $CO_2$  pressure for various silicate-carbonate mineral associations based on data in Robie (1962) and recent values of solubility product of dolomite by Hsu (1963) and Holland *et al.* (1964).

and to fall in slightly carbonated form on dry land. Rain water, often enriched with  $CO_2$  in the soil zone, reacts with silicate and carbonate rocks to produce clay minerals and river water containing largely bicarbonates of  $Na^+$ ,  $K^+$ ,  $Mg^{+2}$ , and  $Ca^{+2}$ . On reaching the ocean, calcium derived from calcite is reprecipitated as calcite or aragonite, the other cations recombine with clays transported by rivers to the sea, and  $CO_2$  is returned to the atmosphere. The oxygen used up in oxidizing reactions in the zone of weathering is produced largely by the reduction of carbonate carbon during photosynthesis to carbon in a valence state near zero. (During metamorphism these reactions are reversed: graphite is used up in the reduction of metals—largely iron—to lower valence states.)

This sort of cycling is, however, not sufficient to account for the leakage of  $CO_2$  from the ocean-atmosphere system into the lithosphere by the precipitation of carbonate minerals containing cations liberated during weathering from noncarbonate minerals. Rubey (1951) has shown that volatiles have almost certainly been added virtually continuously to the surface of the earth, in part via volcanic emanations, in part via hydrothermal solutions.  $CO_2$  has been a major constituent of these volatiles.

The response of the  $CO_2$  content of the atmosphere to the input of  $CO_2$  can be estimated at least roughly. At very low input rates the  $CO_2$  pressure would rise to the values at which  $CaCO_3$  is stable with respect to calcium silicates, quartz, and water. As shown in Figure 2, these pressures are in the vicinity of  $10^{-7}$  atm. The kinetics of weathering processes would probably permit the  $CO_2$  pressure to rise well above  $10^{-7}$  atm, and it is difficult to be sure of the exact amount of overshoot. Between  $10^{-7}$  atm and about  $10^{-4}$  atm, calcium should be removed from the oceans largely as  $CaCO_3$ . But in this pressure interval, magnesium should be removed as hydrous magnesium silicates rather than as dolomite. At  $CO_2$  pressures in excess of  $10^{-4}$  atm, dolomite should become a stable magnesium mineral. The  $CO_2$  pressure at the talc-calcite-dolomite-quartz equilibrium is known only to within about one order of magnitude, and it seems unlikely that this reaction is of importance in water-sediment equilibria. Data for the equivalent reaction with chlorite are not available, but independent data on the solubility product of dolomite (H. D. Holland

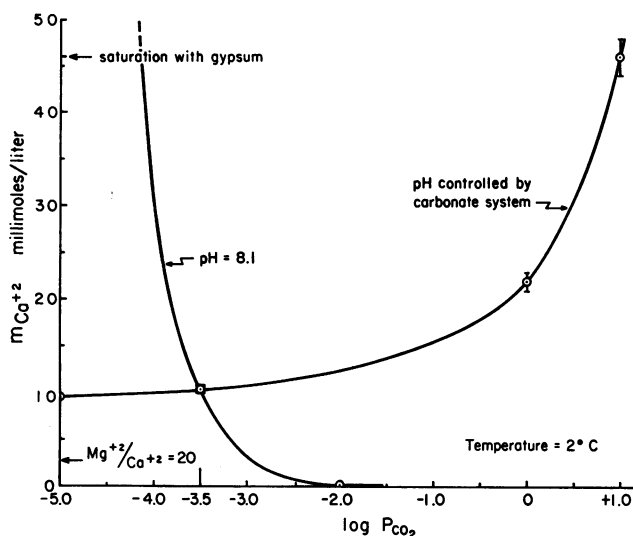


FIG. 3.—The calcium concentration in sea water in equilibrium with calcite as a function of the  $\text{CO}_2$  pressure in the atmosphere; solubility data at 1 and 10 atm  $\text{CO}_2$  were extrapolated from the data of Miller (1952).

*et al.*, 1964; K. J. Hsu, 1963) indicate that present-day sea water is somewhat supersaturated with respect to this mineral. I would like to suggest that the  $\text{CO}_2$  pressure in the atmosphere is being and has been crudely buffered by the coexistence of chlorite, dolomite, calcite, and quartz throughout much of geologic time. The crudeness of the buffering is due in large part to the sluggishness of dolomite nucleation and crystal growth, which is apparently overcome today only in areas of high temperatures and/or abnormally high supersaturation.

In the discussion of controls on the calcium concentration in sea water, it was shown that in a pH-buffered system the product of the  $\text{CO}_2$  pressure in the atmosphere and the activity of calcium in sea water should be nearly constant. This relationship is shown in Figure 3, together with the relationship between calcium concentration and  $\text{CO}_2$  pressure in sea water which is not buffered by clays. If we move along the "buffered" curve to lower  $\text{CO}_2$  pressures, the  $\text{Ca}^{+2}$  concentration of gypsum is exceeded. This mineral is a typical constituent of evaporite deposits but not of normal marine sediments. It therefore seems unlikely that  $P_{\text{CO}_2}$  has been less than  $10^{-4.0}$  atm at least during the recent geologic past.

If we move along the "buffered" curve toward higher  $\text{CO}_2$  pressures, the calcium concentration drops rapidly, and the  $\text{Mg}/\text{Ca}$  ratio increases rapidly. At  $\text{CO}_2$  pressures in excess of  $10^{-3.0}$  atm, this ratio should be as high as in areas of active dolomite formation today. This value of the  $\text{CO}_2$  pressure seems to be near the maximum to be expected until essentially all of the  $\text{Mg}^{+2}$  brought in solution down rivers is precipitated as dolomite rather than as a magnesium silicate.

Carbon dioxide from the earth's interior is accompanied by all of the other "excess volatiles" found in the atmosphere and hydrosphere. Among these, chlorine is of prime importance to oceanic chemistry. As more than 75 per cent of the chlorine added from the interior of the earth is apparently still present in the oceans (W. W. Rubey, 1951), the hydrosphere has acted almost like a simple accumulator system

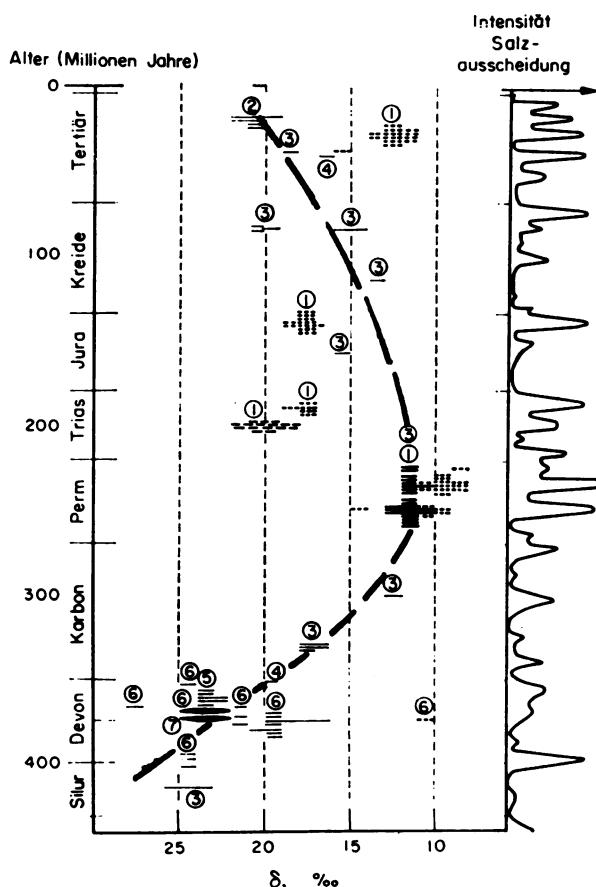


FIG. 4.—The isotopic composition of sulfur in sulfate from evaporite deposits, after H. Nielsen and W. Rieke, 1964.

for both chlorine and water. The chlorinity history of the oceans in the past has therefore been a function largely of the ratio of chlorine to water in the volatiles added to the hydrosphere through geologic time. At present, evidence bearing on the history of this ratio is almost nonexistent. The absence of halite deposits in even unmetamorphosed Pre-Cambrian sediments (F. Lotze, 1964) suggests that perhaps the chlorine/water ratio has increased with time in the volatiles added to the surface of the earth. However, such evidence is very weak, and the consequences of such a change are sufficiently critical to warrant a search for more decisive data bearing on this question.

Even if this ratio has been changing with time, very long periods of time are required to change the chlorinity of ocean water by more than a few per cent. If distilled water were added to the present oceans at the mean geologic rate, about 4 billion years would have to elapse before the salinity of the oceans would drop to half its present value. If water added at the mean geologic rate to the oceans from the interior of the earth were saturated with respect to NaCl, about 500 million years would elapse before the salinity of the oceans would be doubled. Whatever the long-term trends of the chlorinity of ocean water have been, it therefore seems

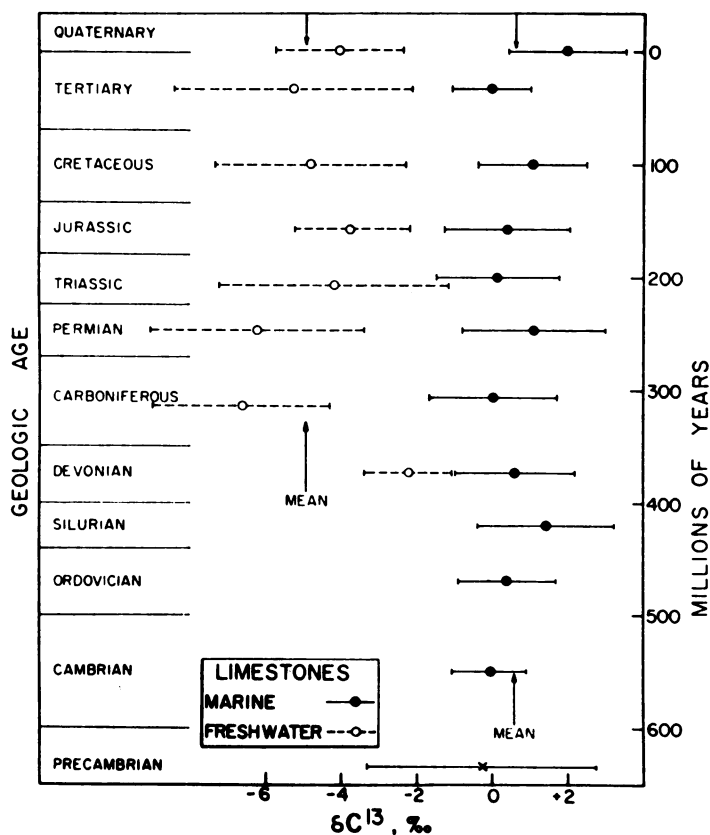


FIG. 5.—The isotopic composition of carbon in limestones (M. L. Keith and J. N. Weber, 1964).

almost certain that during periods of a few hundred million years the salinity of the oceans has changed by less than a factor of 2.

For many of the other volatiles added from the interior of the earth, the atmosphere has been the main accumulation reservoir. This must be essentially true for all of the rare gases except helium, which has been a bird of passage from the earth's interior into interplanetary space (see, for instance, G. J. Wasserberg, 1964). It also seems to be essentially true for nitrogen, despite its present rapid cycling through the biosphere.

It is certainly not true for sulfur which, as sulfate, is the one major component of ocean water that has been mentioned only in passing. Today, ocean water is undersaturated with respect to gypsum and anhydrite, and the removal of sulfate with barite (G. O. S. Arrhenius, 1963) acts as a control on the very small concentration of barium rather than on the concentration of sulfate. The most important mechanism of sulfate removal today seems to be via the bacterial reduction of sulfate to sulfide and sulfur in bottom sediments at the expense of organic carbon (R. A. Berner, 1964). The operation of this mechanism of sulfur removal from ocean water during much of geologic time is strongly supported by the isotopic composition of sulfur in sulfides in sediments of the past 2 billion years (W. U. Ault and J. L. Kulp, 1959). That the ratio of sulfur removal via sulfate precipitation with evap-



orite deposits to sulfide and sulfur removal has varied with time is suggested by the apparent variation shown in Figure 4 of the isotopic composition of sulfur in evaporite sulfates (H. Nielsen and W. Rieke, 1964). But the effect of such fluctuations on the sulfate content of ocean water is difficult to assess. It does, however, seem fairly certain that the activity of sulfate was never so large that the solubility product of gypsum was exceeded in the open ocean, nor so small that gypsum precipitation did not precede the precipitation of halite in evaporite basins.

The much lower oxygen pressure which probably prevailed in our atmosphere during Pre-Cambrian time would have had only an indirect effect on the sulfate balance in sea water. Even in the complete absence of free oxygen, sulfate would have been a stable species in solution (H. D. Holland, 1962), but anoxic bottom conditions were almost certainly much more prevalent in the Pre-Cambrian, and conditions more favorable for bacterial sulfate reduction. The general lack of direct effects of lower oxygen pressures on ocean water chemistry is particularly unfortunate in view of our current attempts to reconstruct the time dependence of the oxygen pressure in the atmosphere.

Perhaps the best indication at present of the relative constancy of the rate of oxygen generation via photosynthesis minus decay of organic carbon comes from the nearly constant isotopic composition, shown in Figure 5, of carbon in marine limestones from the Pre-Cambrian to the present (M. L. Keith and J. N. Weber, 1964). The mean rate of oxygen production via this mechanism is sufficient to account for the accumulation of the oxygen now in our atmosphere (H. D. Holland, 1962). But if most of the oxygen accumulation has taken place since the beginning of the Paleozoic period as suggested by Berkner and Marshall (1964), then large excursions in the past to oxygen pressures higher than 0.2 atm are virtually eliminated by the oxygen requirements for oxidation of surface rocks and of volcanic gases during the last 600 million years.

In the course of this discussion of the controls on the major element composition of the ocean-atmosphere system we have encountered three more or less distinct groups of constituents. The concentration of the first of these is controlled largely by the degassing of the earth, the second by mineral equilibria, and the third by biological reactions. To the first group belong the chloride concentration of sea water and the nitrogen and rare gas content of the atmosphere. To the second group belong the major cation ratios and the pH of sea water as well as the CO<sub>2</sub> content of the atmosphere. To the third belong the oxygen content of the atmosphere and the sulfate content of sea water. The reasonably good equilibration of ocean water with ocean sediment and the very large size of the oceanic reservoir of chloride seem to eliminate more than minor fluctuations in the major element composition of ocean water and in the CO<sub>2</sub> pressure of the atmosphere during periods of time on the order of 10<sup>8</sup> years. Perhaps the greatest contribution of this stability to atmospheric evolution has been the availability of a stable base for the biochemical reactions which seem to have been responsible for the build-up of the oxygen pressure in the atmosphere to its present level.

The contents of this paper have been discussed with many of my colleagues and have suffered improvement on each impact. But I would like especially to acknowledge with thanks the salutary effect of comments by Professors A. G. Fischer, R. M. Garrels, K. S. Deffeyes, P. K. Weyl, W. S. Broecker, K. B. Krauskopf, and P. Bartholomé.

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(Discussion of Dr. Holland's paper)

DR. UREY: Chloride is not a volatile but a soluble . . . [inaudible] . . . . .

FROM THE FLOOR: Would you repeat the comment?

DR. HOLLAND: First, Dr. Urey objects to the use of the term volatile for chloride. Secondly, he feels the major part of the chloride comes from the interior together with sodium.

On the first point, I think it is really a matter of semantics. Rubey classed chloride together with the excess volatiles as one of those things that is present on the surface of the earth in quantities very much larger than can be expected from the weathering of rock.

The second question is very difficult to answer right now. I have racked my brain trying to think of some way to differentiate between chloride that has come out of volcanoes versus what has come out of hydrothermal solutions. I don't know that the distinction is particularly important in terms of the problem at hand, but it would be very nice to know. If you know some way to distinguish the two, I would like to know.

DR. UREY: My only argument was that while the hydrides of the halogens, i.e., HCl, HBr, HF, etc., are gaseous, in terrestrial surroundings they form salts, i.e., CaCl<sub>2</sub>, NaBr, MgF<sub>2</sub>, etc. It is interesting that the soluble ones are concentrated at the surface of the earth, whereas the insoluble fluorides are not.

I don't think this is a matter of semantics. I think it is a matter of purely chemical characteristics.

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## BIOCHEMICAL, BIOLOGICAL, AND ATMOSPHERIC EVOLUTION

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*The Problem.*—There is a close mutual interaction between the evolution of the atmosphere and the early evolution of life. This paper is intended to analyze this interaction relative to its least understood sector: the emergence of the first living systems from the primitive environment.